ORGANIC CARBON FEATURES IDENTIFIED IN THE NAKHLA MARTIAN METEORITE. D.S. McKay¹, K. L. Thomas-Keprta², S. J. Clemett², E.K. Gibson, Jr.¹, L. Le², Z. Rahman², S. J. Wentworth; ¹ARES, NASA/JSC, Mail Code KR, Houston, TX 77058, ²ESCG at NASA/JSC, Mail Code JE23, Houston, TX 77058.

We report, for the first time, the identification of specific carbonaceous phases, present within iddingsite alteration zones of the Nakhla meteorite that possess discrete, well defined, structurally coherent morphologies. These structures bear superficial similarity to the carbonaceous nanoglobules [1] found in primitive chondrites interplanetary dust particles, although they are an order-of-magnitude larger in size.

Introduction: It has been known for many years that some members of the Martian meteorite clan contain organic matter [e.g., 2-4]. Based on both isotopic measurements [5] and circumstantial observations [4] (e.g., the similarity organic signatures present in both Antarctic finds and non-Antarctic falls) a credible argument has been made for a preterrestrial origin for the majority of these organics. The Nakhla meteorite is of particular interest in that it has been shown to contain both an acid-labile organic fraction as well as an acidinsoluble high molecular weight organic component [4]. Pyrolysis-gas chromatography-mass spectrometry of the latter component indicates it to be composed of aromatic and alkyl-aromatic functionalities bound into a macromolecule phase through ether linkages [4]. However, the spatial, textural and mineralogical associations of this carbonaceous macromolecular material have remained elusive [6].

Procedure and Results: Figure 1 shows an SEM image of a freshly fractured Nakhla iddingsite alteration surface. A cluster of salt crystals partially embedded within an underlying microcrystalline layer of iddingsite is surrounded by a second texturally smooth layer of iddingsite. Such layering of iddingsite with differing textures is common in Nakhla [7]. The salt crystals are predominantly halite (NaCl) with the occasional MgCl₂ crystals. Some CaSO₄, likely gypsum, appears to be partly intergrown with some of the halite. EDX mapping shows discrete C-rich features are interspersed among these crystals. We focus here on the hollow semi-spherical 'bowl' structure (~ 3μm Ø) shown in Fig. 2. In order to characterize this feature, a focused ion beam (FIB) was used to cut a transverse TEM thin section of the bowl-shaped feature and the underlying iddingsite (Fig. 3). TEM/EDX analysis reveals that the feature is primarily carbonaceous containing O with lesser amounts of Si, S, Ca, Cl, F, Na, and minor Mn and Fe; additionally a small peak consistent with N is also apparent (Fig. 4). N has been previously documented in Nakhla associated with the stepped combustion of carbonaceous matter [4,8]. While the $F_{K\alpha 1}$ peak often can be overlapped and obscured by the $Fe_{L\alpha}$ peak in EDX analysis, the extremely small $Fe_{K\alpha}$ peak eliminates this overlap problem showing that the F is real and that the C-rich phase contains a significant amount of F. Selected area electron diffraction (SAED) shows that this C-rich material is amorphous. The C-rich feature is intimately associated with both the surrounding halite and underlying iddingsite matrix. TEM/EDX spectra and element maps of the underlying iddingsite show it also contains some C, Si, Fe, Mg, Mn, and O. Except for C, these elements are common in reported iddingsite analyses [9]. In some cases C is spatially associated with Fe and Mg indicating the presence of carbonate grains embedded in iddingsite.

Discussion: Circumstantial evidence suggests this feature (and, by association, other similar C-rich features) are indigenous to the meteorite. The base and extending up one side of the carbonaceous bowl appear to be intergrown both with the underlying iddingsite and with adjacent halite crystals. In some cases, the salt appears to be encrusted on the surface of the features (SEM maps). Both iddingsite and salts are interpreted as having formed as evaporate assemblages from progressive evaporation of water bodies on Mars [10]. This assemblage, sans the carbonaceous moieties, closely resembles iddingsite alteration features previously described which were interpreted as indigenous Martian assemblages [e.g., 11, 12 (& references therein)]. Also, notable is the presence of a significant $F_{K\alpha 1}$ peak consistent with several hundred ppm F. Published F values for bulk subsamples of Nakhla range from ~50-70 ppm and 264 ppm for Mars meteorite Y-00593 [13].

SAED data show the carbonaceous bowl lacks any long range crystallographic order and so is not graphite or carbonate. Micro-Raman spectra acquired from the same surface from which the FIB section was extracted demonstrate a typical kerogen-like D and G band structure with a weak absorption peak at 1350 and a stronger peak at 1600 cm⁻¹. Similar bands are shown from carbonaceous chondrites including Orgueil and Ivuna [14], nanoglobules in Tagish Lake [1], kerogen in 3.4 Ga old Archaean cherts from Australia [15] and in 3.2 Ga old microfossils from South Africa [16].

Conclusion: Here we describe distinctive macromolecular carbonaceous structures in Nakhla that may represent one of the sources of the high molecular weight organic material previously identified in Nakhla [4,8]. While we do not speculate on the origin of these unique carbonaceous structures, we note that the

significance of such observations is that it may allow us to construct a carbon cycle for Mars based on the C chemistry of the Martian meteorites with obvious implications for astrobiology and the prebiotic evolution of Mars. In any case, our observations strongly suggest that organic carbon exists as micrometer-size, discrete structures on Mars.

References: [1] Nakamura K. et al. (2002) Int. J. of Astrobiology 1, 179-189. [2] Wright I.P. et al. (1989) Nature 340, 220-222. [3] Clemett S.J. et al. (1998) Faraday Discuss. 109, 417-436. [4] Sephton M.A. et al. (2002) Planet. Space Sci. 50, 711-716. [5] Jull A.T et al. (2000) GCA 64, 3763-3772. [6] McKay D.S. et al. (2006) LPS XXXVII Abstract # 2251. [7] al.McKay D.S. et(2009) *Proc.* doi:10.1117/12.832317. [8] Sephton M.A. et al. (2000) LPS XXXI, Abstract# 1786. [9] Smith K.L. et al. (1987) Clays and Clay Minerals 35, 418-428. [10] Bridges J.C. & Grady M.M. (2000) EPSL 176, 267-279. [11] Treiman A.H. (1993) GCA 57, 4753-4767. [12] Swindle T.D. & Olsen E.K. (2004) Meteor. Planet. Sci. 39, 755-766. [13] Dreibus G. et al. (2003) LPSC XXXIV, Abstract # 1586. [14] Quirico E. et al. (2005) Planetary and Space Science 53, 1443-1448. [15] Marshall C.P. et al. (2007) Precambrian Res. 155, 1-23. [16] Javaux E. J. et al. (2010) Nature 463, 934-938.

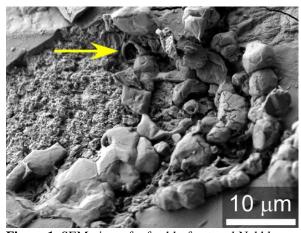


Figure 1. SEM view of a freshly fractured Nakhla surface showing smooth regions (edges of view) of iddingsite with an exposed underlying microcrystalline layer of iddingsite (center of view). Surrounded by and embedded within the microcrystalline iddingsite are salt crystals and several discrete carbonaceous features (some of which are also encrusted by salt). Yellow arrow shows the location of the carbonaceous 'bowl-shaped' feature discussed herein.

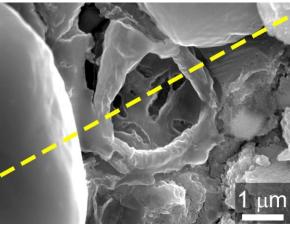


Figure 2. High magnification SEM view of the *C*-rich 'bowl' shaped feature, with yellow dashed line showing the transverse axis along which FIB section was extracted.

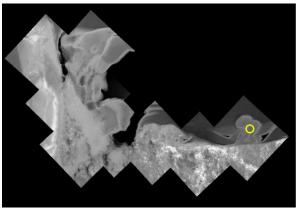


Figure 3. Brightfield TEM view of FIB section through the carbonaceous 'bowl' and the surrounding iddingsite matrix. Yellow circle indicates region from the which EDX spectrum in Fig. 4 was acquired.

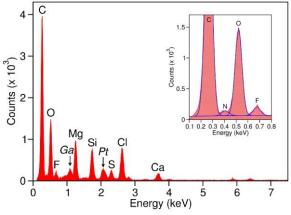


Figure 4. TEM/EDX spectrum of carbonaceous region indicated in Fig. 3, with inset spectrum showing expanded view of 0.1-0.8 keV region and the small peak associated with N.